THESIS

A STUDY OF THE GAS PHASE NITRATION

OF NATURAL GAS

by

James J. Burris

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University of Alberta   July, 1948

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Abstract

      The possibility of producing nitromethane by the atmospheric pressure gas-phase nitration of natural gas has been investigated. The temperature range covered varied from $354^\circ C$ to $455^\circ C$. and the mol ratio of methane to nitric acid varied from 9.6:1 to 26:1. The maximum yield was 33.3 per cent at a temperature of $410^\circ C$., contact time of 2.47 seconds and mol ratio of methane to nitric acid of 18:1.

James Joseph Burris

(May 17, 1924)

Abstract

The possibility of producing nitro-ethane by the atmospheric pressure gas-phase nitration of natural gas has been investigated. The temperature range covered varied from 354°C to 465°C, and the mol ratio of methane to nitric acid varied from 5.6:1 to 20:1. The maximum yield was 33.3 per cent at a temperature of 410°C, contact time of 2.47 seconds and mol ratio of methane to nitric acid of 16:1.

James Joseph Burris

(May 17, 1934)

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Introduction

The recent successful gas phase nitration of
the paraffin hydrocarbons opens up an important new field
in industrial chemistry. The varied and versatile uses of
the nitroparaffins have long been known but expensive pro-
cedures for their manufacture have prevented their wide use.
With the introduction of gas phase nitration the cost of the
nitroparaffins has been lowered to such an extent that their
use in many fields is prophesied.

Nitromethane finds use as an ingredient of solvent
mixtures for nitrocellulose and in the production of chloro-
picrin. The nitroparaffins are also used as inhibitors of
gelling in vulcanizing cements. They are solvents for cellu-
lose acetate, cellulose triacetate, cellulose acetobutyrate,
vinyl resins, nitrocellulose, synthetic resins, dyes, oils,
fats, waxes, and many other organic materials. They are used
in the synthesis of organic compounds including rubber chem-
icals, emulsifying agents, pharmaceuticals, dyestuffs, photo-
graphic chemicals, insecticides, larvicides, wetting agents,
and textile chemicals. The hydroxamic acids which are de-
rivable from the nitroparaffins have found some use as flo-
tation agents for copper ores.

Because of the large potential market for these
products and because of the availability of a cheap source
of high-methane natural gas in Alberta this study was under-
taken. While considerable work has been done in the United
States on the gas phase nitration of paraffins very little

has been reported on the nitration of natural gas.

        The work covered in this thesis involved a comprehensive literature and patent review on the general topic of the gas phase nitration of the paraffins with particular emphasis on methane. A simplified nitrating apparatus was constructed and the effect of mol ratio and temperature on yield at constant contact time were studied.

Literature Review

Work carried out at Purdue University by Hass and co-workers on the gas phase nitration of paraffin hydrocarbons and reported in 1934 (P2) was the beginning of a series of studies that resulted in the successful nitration of butane, isobutane, propane, ethane and methane. The gas phase nitration of ethane, propane, butane and isobutane were carried out without much difficulty. Methane however proved to be more difficult, and the first attempts to nitrate this gas failed. Landon (P4) of the research staff of the Hercules Powder Company first reported the successful nitration of methane.

Hass, Hodge and Vanderbilt prepared nitromethane, nitroethane, both nitropropanes and all four nitrobutanes by the nitration of isobutane, butane and propane at $420^\circ C$. They reported that the ratio of isomers in the reaction products is controllable (3). The effects of various modifications of the nitration procedure were also reported. When air or free oxygen is added to the nitration mixture the oxidation reaction is favored with no increase in the nitration. This is probably because the equilibrium

$$4 \ HNO_3 \rightleftharpoons 4 \ NO_2 + 2H_2O + O_2$$

is displaced completely to the right at these temperatures and the only reason that nitric acid is present is that it has not had time to decompose.

The yield of nitroparaffin was found to increase with increasing hydrocarbon concentration in the inlet gases

until the ratio is about 14 to 1, after which there is little or no effect.

Hass and co-workers nitrated n-pentane at 400°C. obtaining the following nitroparaffins, 1-nitropentane, 2-nitropentane, 3-nitropentane, 1-nitrobutane, 1-nitropropane, nitroethane and nitromethane (4).

The nitration of isopentane was carried out at two temperatures 380°C. and 420°C. (12). The average yield per pass based on the nitric acid added was 17.5 per cent. The average mole ratio of hydrocarbon to acid was 1.71. At 420°C. the average yield per pass was 23.5 per cent, and the average mole ratio of hydrocarbon to acid was 4.73.

Hibshman, Pierson and Hass carried out work on the nitration of ethane (8). A maximum conversion of 33 per cent was obtained with a contact time of 0.33 seconds and a temperature of 455°C.; a temperature of 475°C. was required to give the maximum conversion of 32 per cent with 0.23 seconds exposure time. The 50 per cent nitric acid used in this investigation contained 3 grams/litre of dissolved potassium nitrate. There was some retention of the salt in the reaction chamber which had a beneficial effect. The salt film aided the nitration reaction, probably by masking the catalytic effect of the stainless steel walls on the competitive oxidation reaction.

The conversion of acid to nitroparaffin increased with an increase in mole ratio up to an ethane-nitric acid

ratio of 10 to 1; above that value further increases had little effect. At mole ratios below 10 to 1 the reaction temperature control was poor, and it is probable that the low conversions accompanying low hydrocarbon excesses are somewhat attributable to this lack of temperature control. With a contact time of 0.30 - 0.33 seconds, bath temperatures above 450°C. were attended by poor temperature control.

Analyses of the exit gases of a vapor-phase nitration have indicated that the elemental nitrogen content is never greater than 5 per cent of the nitric acid which is passed through the reactor. The balance of the nitrogen appears as nitroparaffin or as oxides of nitrogen. If provision were made to reconvert the nitrogen oxides to nitric acid, the conversions of 32 per cent would correspond to a yield of about 90 per cent, based on the formation of nitroparaffin from nitric acid.

Since considerable success was achieved by using nitric acid as a starting medium for the nitration of paraffins attention was concentrated on the advisability of using nitrogen dioxide as the nitrating agent. Hass, Dorsky and Hodge (5) made a study of the conditions of temperature and contact time best suited for the production of the nitroparaffins from nitrogen dioxide and propane over a wide temperature range. The mole ratio of hydrocarbon to NO$_2$ was maintained as closely as possible to 4:1. This mixture was

found to be non explosive. Over the range of reaction
temperatures studied from 600°C. to 425°C. the maximum
conversion varied from 4 per cent at the highest to about
9 per cent at the lowest. The conversion increased from
6.6 per cent at a contact time of 0.725 minutes to 26 per
cent at 14.2 minutes.

The vapor phase nitration of propane with nitro-
gen dioxide produced a mixture of nitroparaffins along with
other products which presumably resulted from the simultan-
eous oxidation and cracking reactions. High temperatures
favored the formation of the by-products such as aldehydes,
olefins and carboxylic acids resulting from the side re-
actions. At the contact time necessary for maximum conver-
sion even at 248°C. the oxidation reaction was still appre-
ciable. This was evidenced by the fact that 5 per cent of
the reaction product at this temperature consisted of
aldehydes. In some of the runs at high temperatures a white
crystalline substance separated out in the condensing system.
The crystals were identified as ammonium nitrate, and their
presence indicates that ammonia was formed during the re-
action.

The relative proportions of the various nitro-
paraffins produced, varied with the reaction temperature.
This variation was in accordance with the observation that
high temperature favors the formation of the lower nitro
compounds (nitromethane and nitroethane) and primary substi-

tution products (l-nitropropane) at the expense of secondary
and / or tertiary isomers (2-nitropropane).

Nitrogen dioxide and nitric acid yield the same
nitroparaffins although conversions are lower with the
former reagent.

Landon, of the Hercules Powder Company, nitrated
methane in the gas phase using a reaction vessel having a
ferrous inner surface with a ratio of surface area to vol-
ume less than that of a $\frac{1}{4}$ inch tube (P4). The range of
temperature varied from 375° to about 550° at a contact
time in the reaction zone within the range of about 1.0 sec-
onds to about 0.005 seconds. The reaction mixture was rapid-
ly removed from the reaction zone and cooled.

In the nitration of paraffins, the production of
nitromethane has presented acute problems due to low con-
versions and difficulty in recovering the unreacted methane
to permit its recycling to the nitrator. Rideout (P8) has
shown that these problems can to a large extent, be obviated
by using a single pass nitration wherein the methane is
diluted by a recirculated inert gas such as nitrogen. When
the methane content of the gas mixture is reduced to about
10 to 15 per cent, relatively high yields of nitromethane
are obtained.

Boyd and Hass (1) reported on the nitration of
methane at atmospheric pressure, the nitromethane being form-
ed by the direct reaction of co-mingled streams of CH_4 and

of HNO_3 in CO_2 and steam. The nitric acid used had a con-
centration of 67 per cent and the reaction temperatures
ranged from 375°C. to 600°C. The most favorable conditions
found using a ratio of 9 moles of methane to 1 of nitric
acid, are a temperature of 475°C. and an exposure time of
0.18 seconds. The optimum conversion of nitric acid to
nitromethane was 13 per cent per pass.

A run with natural gas containing ethane always
yields more than the proportional amount of nitroethane in
the nitrated product since the yield of this nitroparaffin
per pass is almost three times that of nitromethane. It
was shown that when the mol ratio of hydrocarbon to nitric
acid exceeds 9 to 1, there is no appreciable effect on the
yield from the reaction.

Hass, Shechter, Alexander and Hatcher (6) deter-
mined the effect of pressure on the gas phase nitration of
methane. Their work was carried out in a pyrex reactor at
low pressures and in a 18-8 stainless steel vessel at high
pressures. These authors state that reactors constructed from
glass tubing of large diameter give low conversions of nitric
acid to nitromethane.

A maximum conversion of 16.4 per cent was obtained
in pyrex tubing having an outside diameter of 7 mm., whereas
a conversion of 12.2 per cent resulted from an experiment
conducted under similar conditions in a reactor constructed

from glass tubing with an outside diameter of 25 mm. These
results indicated to the authors that reactors having a large
ratio of surface area to volume are necessary to control
the reaction temperature.

No appreciable effect on reaction yields was ob-
served by using nitric acid ranging in composition from 40
to 70 per cent HNO_3.

It was concluded that the nitration reaction at
a gauge pressure of 100 pounds per square inch is difficult
to control and that a mol ratio of methane to nitric acid
of at least 10:1 must be maintained to obtain good yields.
The nitration yield is increased by raising the pressure to
100 pounds per square inch, but no great advantage is to be
gained by using higher pressures. A maximum yield of 27.2
per cent was reported at a pressure of 100 pounds per square
inch at an exposure time of 0.75 seconds and a temperature
of $444^{o}C$.

Some work has been done on methods of recovering
the products formed in the reaction and the recycling of
the unreacted portion. Kieweg (P3) reports on a method for
the recovery of lower nitroalkanes from the gaseous products
of vapor phase nitration of lower alkanes by HNO_3 or NO_2 at
elevated temperatures. The lower nitroalkanes in the gaseous
reaction products are absorbed by bringing the reaction pro-
ducts into contact with silica gel.

Jerome Martin and E. B. Hodge (P7) developed a

cyclic process for the nitration of the lower alkanes which
involve removing lower nitroalkanes from the gaseous mix-
ture resulting from the nitration reaction, and subjecting
the remaining gases to scrubbing with an aqueous medium to
remove substantially all the aldehydes and ketones, and
introducing the resulting gases into the reaction mixture
for the suceeding cycle.

Nitromethane is the only mononitroparaffin which
can be detonated with a cap (3) but the homologous mono-
nitroparaffins may explode when heated in a closed container
under pressure (11).

Nitroparaffins have a characteristic, mild, not
unpleasant odor usually described as chloroform-like. They
are entirely colorless when pure. Further properties of
nitromethane are given in the appendix.

The nitroparaffins have many potential industrial
uses. As long ago as 1907 Fischer (P1) patented the use of
nitromethane as a solvent for cellulose nitrate and cellulose
acetate.

Nitromethane is also a surprisingly reactive com-
pound as can be seen by referring to the nitromethane tree
in the appendix.

Loomis (P6) has patented the use of nitroparaffins
as a priming compound in diesel fuels.

Theory

The liquid-phase nitration of paraffinic hydro-
carbons is confronted with certain inherent difficulties.
Nitric acid and the alkanes are mutually insoluble, whereas
the nitrated product is considerably more soluble in the
nitric acid layer and is there subjected to further nitration,
hydrolysis and oxidation. These particular difficulties may
be removed by operating in the vapor phase. The reactants .
may then be mixed in any desired proportions, and since the
reaction is almost instantaneous, practically no polynitro
derivatives are formed.

Wenner (13) has shown from the equation and free
energy data given as follows, that the nitration of methane
is accompanied by a free energy decrease at all temperatures.
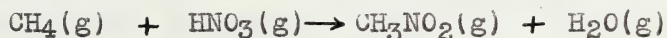
$$CH_4(g) \;+\; HNO_3(g) \longrightarrow CH_3NO_2(g) \;+\; H_2O(g)$$
$$\Delta F^{O} = -25,975 - 5.76\,T$$

Since methane cannot be nitrated at low tempera-
tures it is apparent that the yield from this reaction is
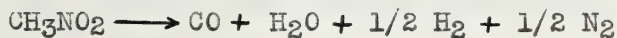limited by catalytic and kinetic factors.

Along with nitration the following oxidation and
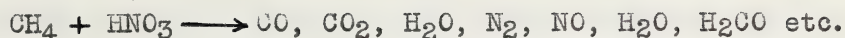decomposition reactions may occur -

$$HNO_3 \longrightarrow 1/2\,H_2 + 1/2\,N_2 + 3/2\,O_2$$
$$\Delta F^{O} = 0 \text{ at approx. } 394^{O}C.$$

$$2\,HNO_3 \longrightarrow 2\,NO + 3/2\,O_2 + H_2O$$
$$\Delta F^{O} = 50,370 - 93.4\,T$$

$$CH_3NO_2 \longrightarrow CO + H_2O + 1/2\,H_2 + 1/2\,N_2$$
$$\Delta F^{O} = -66,500 - 3\,T \ln T - 34\,T$$

$$CH_4 + HNO_3 \longrightarrow CO, CO_2, H_2O, N_2, NO, H_2O, H_2CO \text{ etc.}$$
$$\Delta F^O = \text{negative}$$

The mechanism of vapor phase nitration has been studied by McCleary and Degering (10). Their results indicate that the alkanoic acids are not intermediates and that addition complexes and / or free radicals or both may account for the reaction products. The production of optically-active nitroalkanes seems to preclude the possibility of free radicals, since free radicals would yield racemic mixtures. The activated intermediate, therefore, may be assumed to be a momentary addition complex between the hydrocarbon and the nitric acid. This intermediate subsequently loses water.

Both the nitration reaction and the competing oxidation reaction are exothermic.

Hibshman, Pieron and Hass (8) have shown that the nitration is a homogeneous gas phase reaction.

Since the reaction has an activation energy of 52 cals./mol it is preferentially accelerated by an increase in temperature. Elevated pressures increase the reaction rate and the difficulty of temperature control without greatly increasing the yields (6).

Catalysts accelerate the oxidation reaction rather than the nitration one. Silica gel, nitric oxide, platinum oxide, iron, copper, lead and the heavy metal oxides catalyze oxidation and thus result in poor yields of nitroparaffins,

whereas light, aluminum nitrate or carbon monoxide have no appreciable effect. However it has been found that the chromium-nickel steels which resist the corrosive reaction of nitric acid at high temperatures will not greatly effect the oxidation and decomposition reactions if a mixture of sodium and potassium nitrate is sprayed continuously into the reactor (7). A silicate catalyst containing arsenic or antimony or both is reported to improve the yield of nitroparaffins (P5).

Materials

Natural gas from the Kinsella and / or Viking gas field, available in the city service lines, was used as the hydrocarbon source. This gas has the following composition :

Methane	93.90%
Ethane	0.86%
Carbon dioxide	0.10%
Oxygen	0.13%
Nitrogen	5.0 %

It was found convenient throughout this study to consider the natural gas as methane plus inerts, the inerts consisting of carbon dioxide, oxygen and nitrogen.

The nitric acid used was 71.7 per cent. This acid was filtered through glass wool before using.

Apparatus

The apparatus for the gas phase nitration of
natural gas was designed for continuous uniform flow of
both gas and nitric acid into a reactor in a molten salt
bath maintained at a controlled temperature. A series of
condensers and a caustic scrubber completed the flow system.
A detailed description follows.

Referring to Figure 1, natural gas was admitted
from the service line and passed through a calibrated
orifice manometer. From here it passed to a mixing column
where it came in contact with the nitric acid.

The nitric acid is held in a 500 c.c. dropping
funnel which has the stem drawn out to a small opening. A
calibrated glass capillary dropper is attached to the drop-
ping funnel by means of a short length of rubber tubing.
Care was taken that glass to glass contact be maintained in
order to prevent any action between the acid and rubber.
The dropper was so arranged that the acid would run down the
mixing tube and would be completely vaporized before reach-
ing the reaction chamber.

The mixing tube reaches down approximately half
way into the reaction vessel. A thermometer was inserted
in the reaction zone with its bulb slightly above and to
one side of the end of the mixing tube.

The reaction vessel is a 250 c.c. pyrex distilling
flask which is immersed in a molten salt bath up to the point
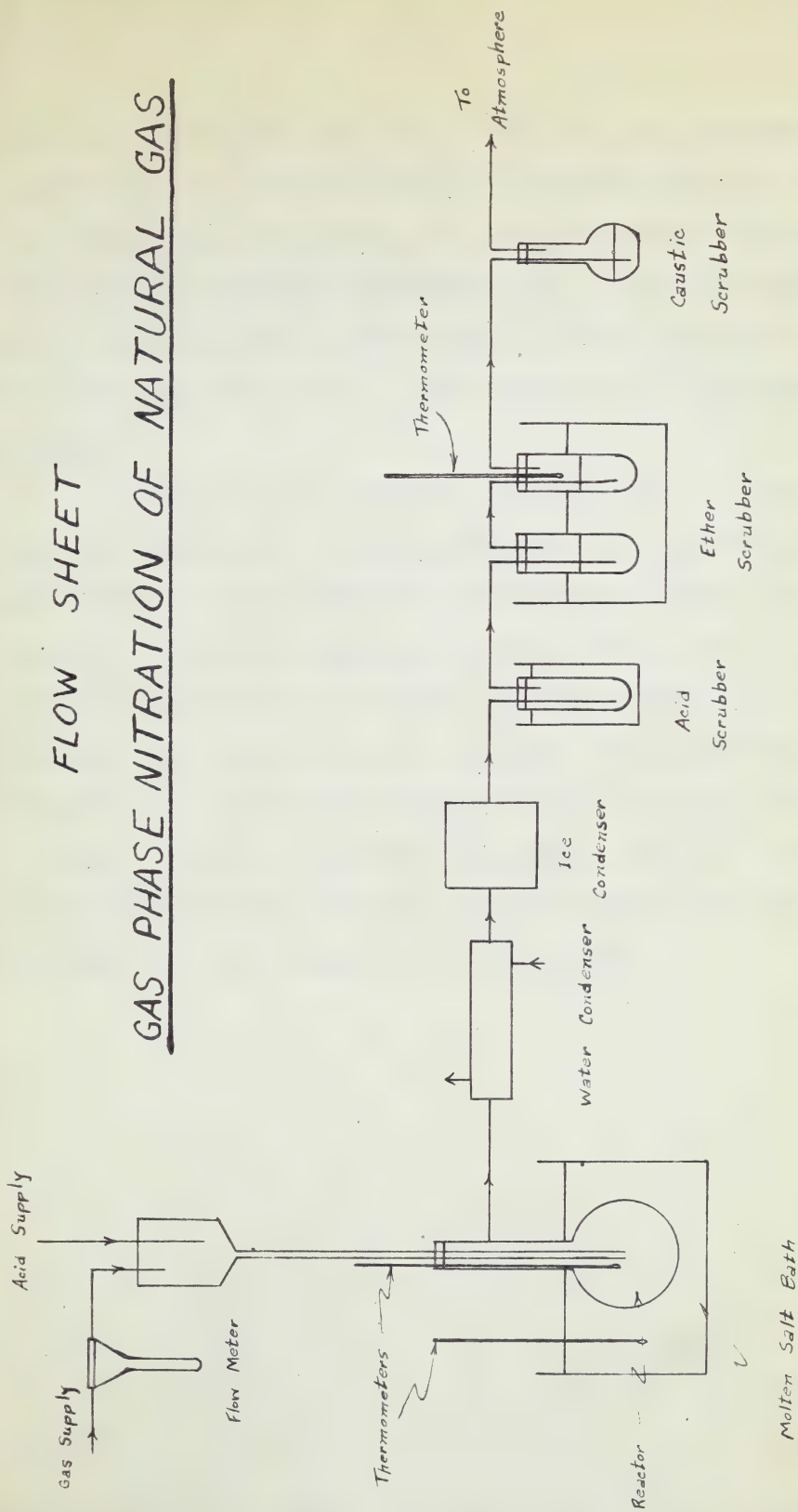
FLOW SHEET

GAS PHASE NITRATION OF NATURAL GAS

FIGURE 1

where the bulb meets the stem. The salt bath has the following composition, 40 per cent $NaNO_2$, 7 per cent $NaNO_3$ and 53 per cent KNO_3. This composition was chosen because of its great stability at elevated temperatures (9). The salt bath is heated with gas and is controlled by means of a gas thermometer type of controller. This controller is illustrated in Figure 2.

The reaction products pass through a counter-current water condenser, and an ice condenser. A scrubber packed with glass wool and saturated with concentrated nitric acid, immersed in a salt-ice mixture follows. From here the reaction products which have not already condensed pass to a scrubber immersed in a acetone-dry ice mixture. This scrubber consists of two 50 c.c. test tubes each of which contained 20 c.c.'s of ether. A caustic scrubber containing 100 c.c. 's of approximately 1N KOH completes the flow system and from here the remaining gas passes to the atmosphere.
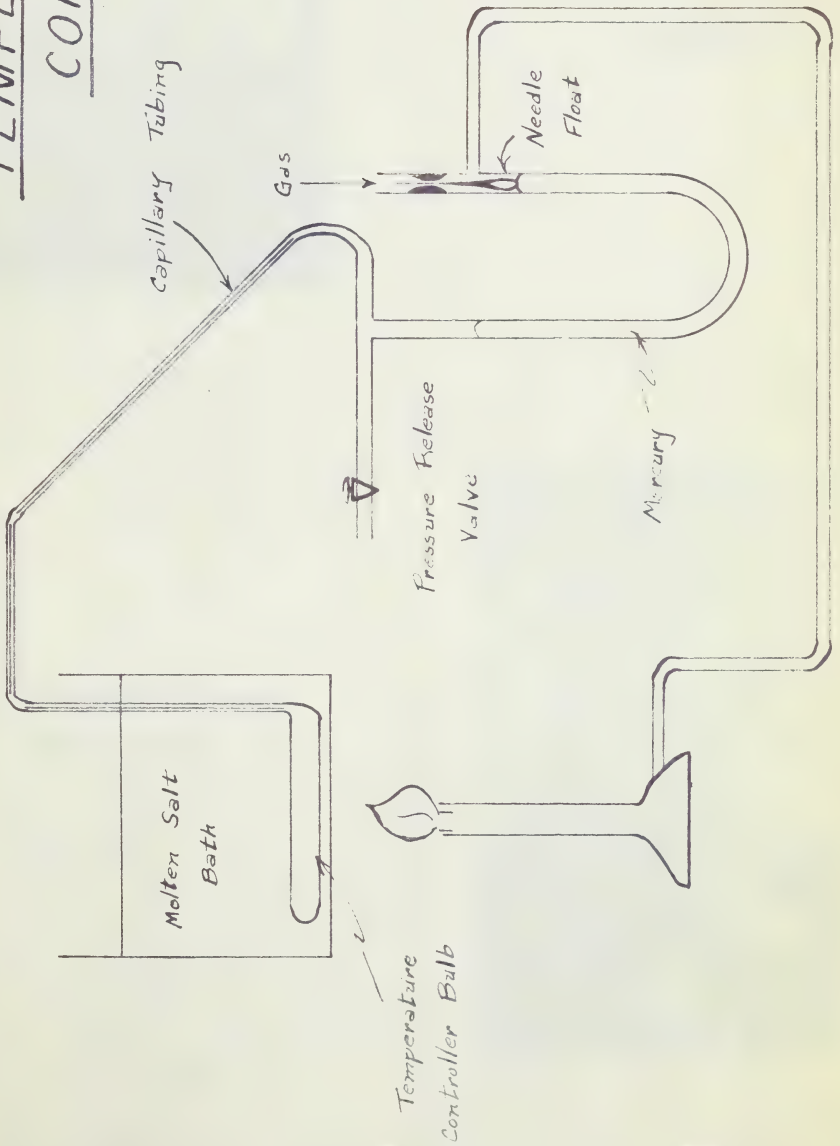
TEMPERATURE CONTROLLER

FIGURE 2

Nitration Apparatus
Front View
Figure 3

Nitration Apparatus
Side View-showing
condenser system
Figure 4

Experimental Procedure

The salt bath was allowed to come up to tempera-
ture well in advance of the run. Shortly after the salt
bath became molten the gas thermometer bulb and the reaction
vessel were placed in the bath. The thermometers were then
placed in the salt bath and in the reactor. As soon as the
bath reached a temperature about ten degrees below that de-
sired the pressure release valve on the temperature controller
(see Figure 2) was closed. This resulted in the desired
temperature being maintained.

After the remainder of the apparatus was set up all
cork stoppers were sealed with wax. The connections through-
out are all glass to glass. The gas was then allowed to pass
through the apparatus with a manometer reading maintained at
2 cms. This corresponds to a methane rate of .0142 lb. mols
per hour. With the gas running through the apparatus a check
was made for leaks.

When the apparatus is in working order and the gas
passing through at a constant rate the nitric acid was allow-
ed to pass into the reaction chamber and a timer was started.
The acid dropper is so arranged that the drops do not fall
directly into the reactor but flow down the stem of the mix-
ing tube connecting the dropping funnel to the reactor. This
results in a more evenly distributed flow into the reaction
vessel. The acid becomes vaporized in its flow downward and
mixes with the gas.

During each run the following readings were taken
every ten minutes: acid dropping rate, gas flow rate, bath
temperature, reaction temperature and temperature of the
gas leaving the ether scrubber. After an interval of one
hour the nitric acid flow was stopped. The gas however
was allowed to pass through the apparatus for another two
minutes to flush it out. The various condensers and scrub-
bers were then removed and the products analysed for nitro-
methane.

Since the loss of nitromethane in the extraction
procedure is cumulative and difficult to determine directly
a standardization run was made using a known amount of nitro-
methane and maintaining conditions as nearly similar to
operating conditions as possible. No nitric acid was passed
through the apparatus in this standardization run.

Analytical Methods

The nitromethane which constitutes the desired product from this reaction is obtained from three sources. The major portion of this product is found in the ether scrubber. The ether is distilled off in a water bath, the bath temperature not being allowed to exceed 55°C. A small amount of boric acid was added to prevent any decomposition of the nitromethane. The acid is neutralized with approximately 10N KOH and the product is separated from the saturated salt solution layer. The amount of nitromethane remaining in the saturated salt solution was determined since its solubility is known. This was found to be 2.8 c.c.'s per 100 c.c.'s of solution under the experimental conditions.

The product from the ice condenser and the scrubber immediately following it contains mainly water and unreacted nitric acid plus a small amount of nitromethane. This is neutralized with approximately 10N KOH until a slight orange color is imparted to the solution. This occurs at a pH of about 5 as determined with congo-red paper. This neutralized solution was then extracted with ether.

The product from the caustic scrubber was neutralized with concentrated nitric acid. This neutralized solution was also extracted with ether.

Method of Calculation

Contact Time

The contact time was computed from the inlet gas volume, corrected to the reactor temperature and pressure. The bulb volume used in determining the time of contact was 280 c.c.'s. All contact times are expressed in seconds. A sample calculation is as follows:

$$\frac{280}{28,320} \quad x \quad \frac{3600}{13.20} \quad = \quad 2.70 \text{ seconds}$$
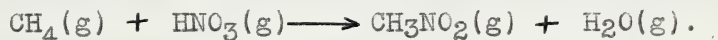
where 13.20 is the gas volume in cubic feet per hour passing through the reactor at $354^{\circ}C$. and 710 mm. Hg pressure.

Capillary Dropper Calibration

The capillary droppers were calibrated by weighing the amount of nitric acid which passed through the dropper in one minute. The number of drops per minute were also determined.

Yields

The theoretical yield of nitroparaffin calculated as nitromethane was determined by use of the following equation in which 63 grams of nitric acid theoretically results in a nitromethane yield of 61 grams.

$$CH_4(g) + HNO_3(g) \longrightarrow CH_3NO_2(g) + H_2O(g).$$

Experimental Results and Discussion

On the first few runnings of the nitration ap-
paratus a simple condenser system was used consisting of a
water condenser, ice condenser and a dry ice-acetone con-
denser. The yields using this condenser system were low
and it was suspected that considerable nitromethane was
passing out with the exit gases. This loss was substan-
tiated by placing a caustic scrubber containing a 10 per
cent solution of KOH in the flow circuit. After the com-
pletion of the run this solution was a bright red color.
As a result the flow system was changed to the one described
earlier in this report.

Even using an ether scrubber all the nitromethane
was not removed thus necessitating a caustic scrubber in the
flow circuit as shown in Figure 1. Here the nitromethane
was tied up as the potassium salt.

The major portion of the nitromethane produced was
trapped in the ether scrubber along with some nitric acid
and nitrogen trioxide. The collector in the ice condenser
contained mainly unreacted acid and water plus a small a-
mount of nitromethane. The distribution of the nitromethane
is shown in Table II.

Effect of Temperature on the Reaction

The reaction temperatures and bath temperatures
remained quite constant during the runs.

The temperature was found to be fairly critical in
the gas phase nitration of methane. In all cases observed

TABLE I

Experimental Data and Results

Methane Flow Rate ....0.0142 lb.mols per hour
Pressure....710 mm. Hg
Duration of run....60 minutes
Contact Time....2.38 - 2.70 seconds (440°C. - 354°C.)
Nitric Acid Concentration....71.7%
Extraction Efficiency (from standardization run)....96%

Run No.	Mols CH_4 per Mol HNO_3	Bath Temp. °C.	React Temp. oC.	Ether Scrubber Temp. °C.	Acid Used gms.	Theor. Yield gms. #	Act. Yield Corrected gms. ##	% Yield
1	25.4	380	368	-68	15.4	14.9	3.44	23.2
2	24.4	396	388	-65	16.6	16.1	4.39	27.3
3	25.4	413	412	-63	15.9	15.4	5.00	32.4
4	26.4	434	435	-66	15.3	14.8	2.50	16.2
5	26.4	395	391	-65	15.3	14.8	4.39	29.6
6	26.4	427	426	-63	13.8	13.4	3.68	27.5
7	30.5	391	381	-70	13.3	12.9	4.03	31.2
8	27.0	439	438	-68	14.9	14.5	3.08	21.2
9	18.8	370	354	-70	21.5	20.8	4.17	20.0
10	16.9	376	368	-69	23.9	23.2	6.17	26.6
11	18.8	383	371	-70	21.5	20.8	5.46	26.2
12	18.5	400	390	-69	21.9	21.2	6.88	32.4
13	18.8	416	390	-69	19.7	19.1	5.83	30.4
14	17.2	434	440	-41	23.4	22.7	5.60	24.7
15	17.5	408	409	-64	23.1	22.4	7.48	33.3
16	17.7	424	430	-64	22.8	22.1	6.40	28.9
17	10.4	393	384	-66	39.0	37.8	3.68	9.7
18	9.8	418	420	-63	41.0	39.7	5.94	15.0
19	10.7	400	416	-56	38.0	36.8	4.75	12.9
20	7.6	441	455	-60	32.2	31.2	2.50	8.0

\# Based on nitric acid used.
\## Actual Yield Corrected = Actual Yield x $\frac{100}{96}$

TABLE II

Nitroparaffin Distribution

Run No.	CH_3NO_2 in Condenser System c.c.'s	CH_3NO_2 in Ether Scrubber c.c.'s	CH_3NO_2 in Caustic Scrubber c.c.'s	Total Volume c.c.'s	Total Weight gms.	Total Weight Corrected gms. #
1	0.4	2.3	0.2	2.9	3.30	3.44
2	0.2	3.1	0.4	3.7	4.22	4.39
3	0.6	3.0	0.6	4.2	4.79	5.00
4	0.4	1.3	0.4	2.1	2.40	2.50
5	0.4	3.0	0.3	3.7	4.22	4.39
6	0.2	2.7	0.2	3.1	3.54	3.68
7	0.2	3.0	0.2	3.4	3.88	4.03
8	0.6	1.4	0.6	2.6	2.96	3.08
9	0.4	1.7	1.4	3.5	4.00	4.17
10	0.2	3.9	1.1	5.2	5.93	6.17
11	0.6	3.8	0.2	4.6	5.25	5.46
12	0.9	4.7	0.2	5.8	6.61	6.88
13	0.4	3.9	0.6	4.9	5.58	5.83
14	0.8	3.4	0.5	4.7	5.36	5.60
15	0.8	4.3	1.2	6.3	7.19	7.48
16	0.8	3.4	1.2	5.4	6.15	6.40
17	0.6	2.3	0.2	3.1	3.54	3.68
18	1.2	2.9	0.9	5.0	5.70	5.94
19	1.6	2.1	0.3	4.0	4.56	4.75
20	0.6	0.9	0.6	2.1	2.40	2.50
Stand. Run	0.6	2.0	0.5	3.1	3.55	

Initial amount of CH_3NO_2 = 3.70 gms.

\#   Total Weight Corrected = Total Weight x $\dfrac{100}{96}$

the optimum temperature for the reaction was approximately
410°C., the yields falling off rapidly as the reaction
temperature increased or decreased. Figure 5 illustrates
this graphically.

Preliminary runs have established that no nitra-
tion reaction occurs below 335°C.

The variation of the reaction temperature with
bath temperature is shown in Figure 6. These results
illustrate the exothermic nature of the reaction, the salt
bath serving as a heating medium at the lower temperatures
and a cooling medium at higher temperatures.

A strong blue color was imparted to the ether so-
lution at low reaction temperatures due to liquid N_2O_3 which
dissolved in the ether. On removing the ether solution from
the dry-ice acetone bath brown NO_2 fumes came off as the
N_2O_3 was oxidized by the air.

The maximum yield based on the nitric acid used,
occurring at a reaction temperature of about 410°C., and
contact time of 2.47 seconds was 33.3 per cent using a mol
ratio of methane to acid of 18:1, 32.6 per cent with a mol
ratio of 26:1 and 14.0 per cent with mol ratio 9.6:1.

Effect of Mol Ratio on the Reaction

No advantage is to be obtained by operating at a
mol ratio of methane to acid greater than 18:1. A mol ratio
of 9.6:1 resulted in low yields. The optimum mol ratio to
be used with contact time 2.38—2.70 seconds is probably be-
tween these two values. There is no great difference in

FIGURE 5

EFFECT OF TEMPERATURE ON YIELD

Mol Ratio 18/1

Mol Ratio 26/1

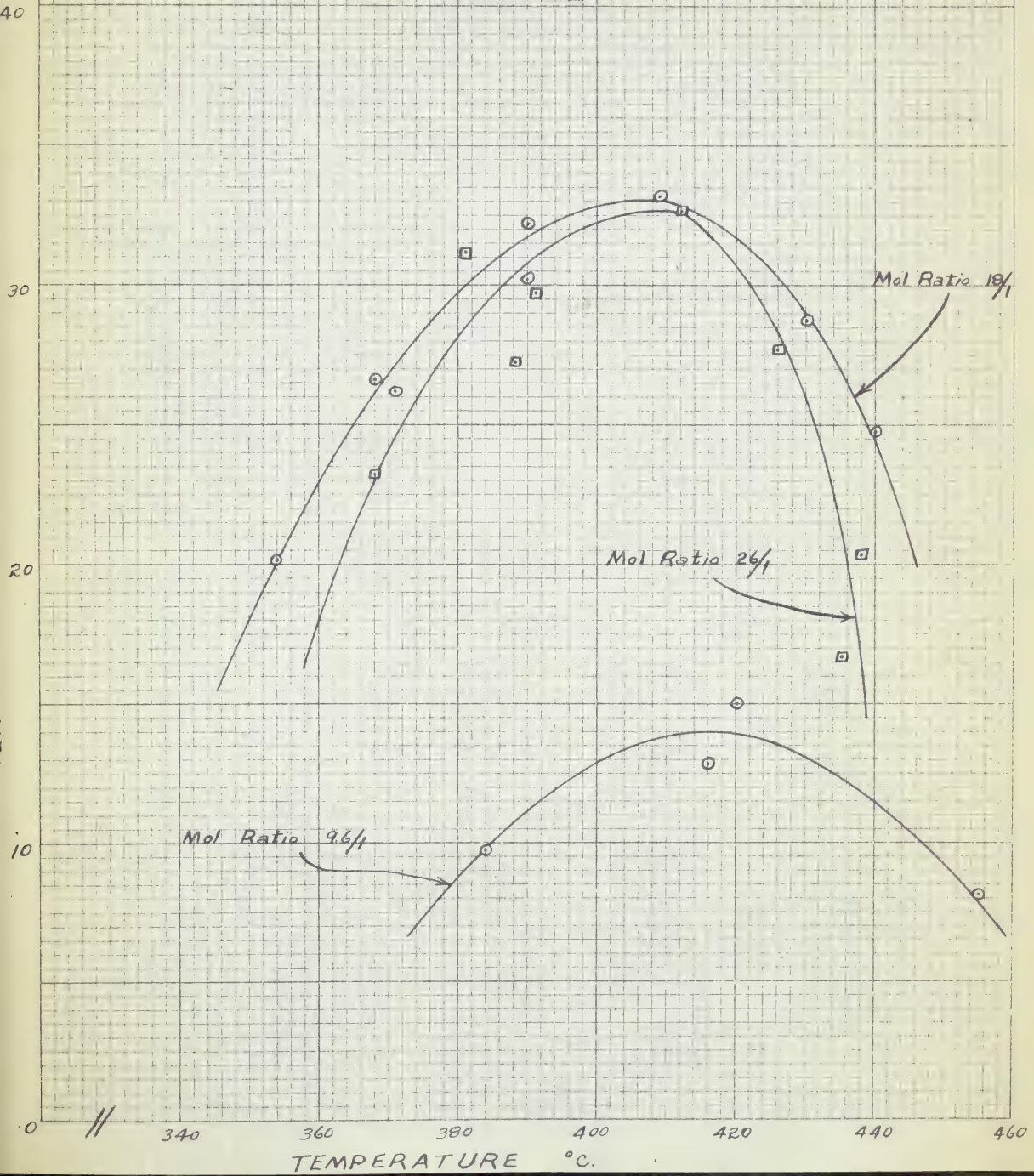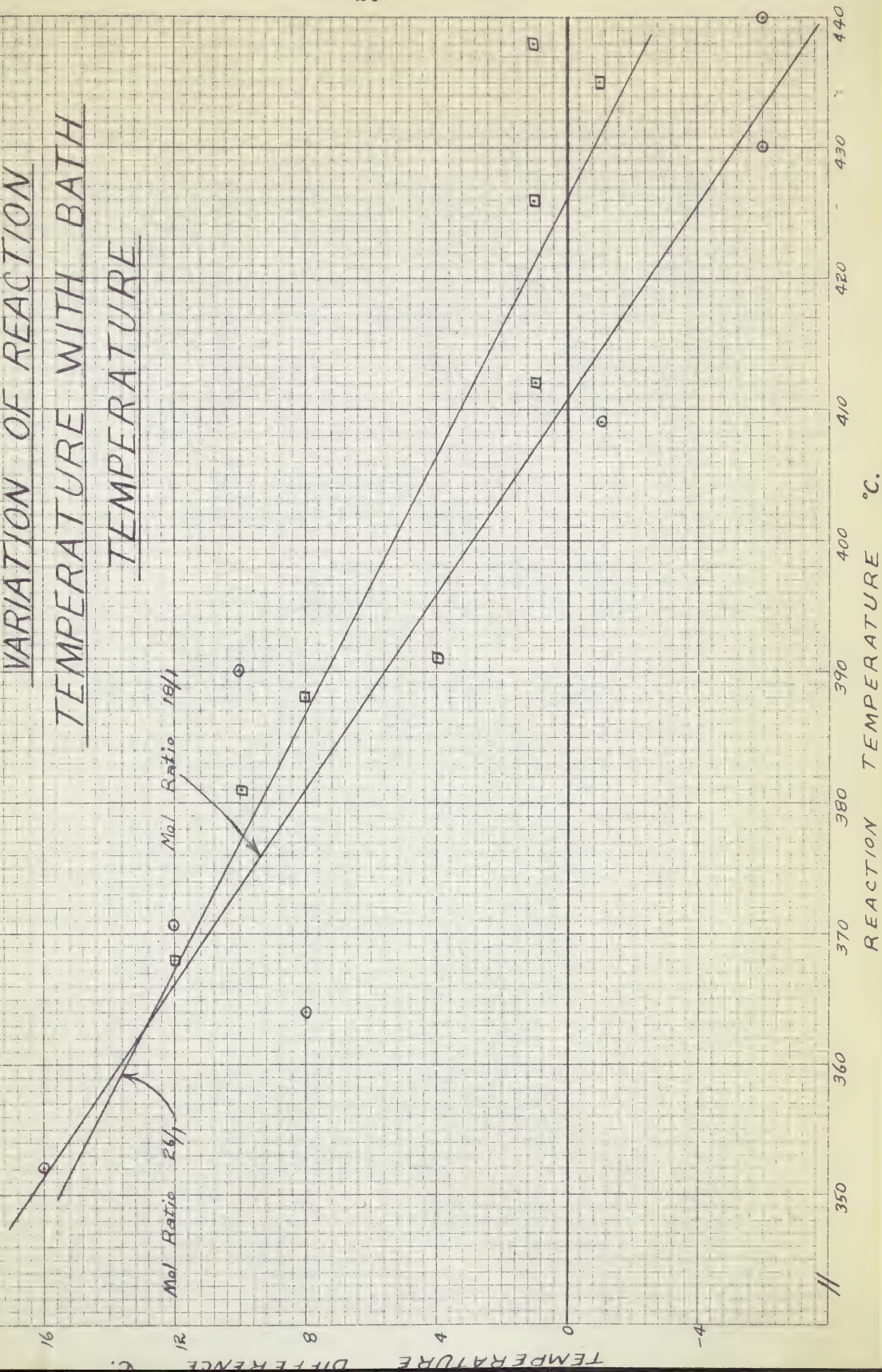Mol Ratio 9.6/1

TEMPERATURE °C.

FIGURE 6

VARIATION OF REACTION
TEMPERATURE WITH BATH
TEMPERATURE

the two curves of Figure 5 representing mol ratios of
18:1 and 26:1, both having a maximum at the same tempera-
ture and having the same general shape.

Summary

The possibility of producing nitromethane by the atmospheric pressure gas-phase nitration of natural gas has been investigated. The following ranges of conditions have been covered:

Temperature: $354^{\circ}C. - 455^{\circ}C.$

Mol Ratio CH_4/HNO_3 : 9.6:1 — 26:1

Results indicate the following:

1. Reaction is exothermic.

2. No appreciable nitration reaction occurs below $335^{\circ}C.$

3. Mol ratios of methane to nitric acid above 18:1 do not result in increased yield.

4. The optimum temperature for the reaction at a contact time of 2.47 seconds is approximately $410^{\circ}C.$

5. The maximum yield of nitromethane based on the added nitric acid is 33.3 per cent at a temperature of $410^{\circ}C.$, contact time of 2.47 seconds and mol ratio of methane to acid of 18:1.

APPENDIX

FIGURE 7

Nitromethane Tree (2)

Part I

CH_3NO_2

| HCHO | 2HCHO | 3HCHO | C_6H_5CHO |

$CH_2OH - CH_2NO_2$ $(CH_2OH)_2CHNO_2$ $(CH_2OH)_3CNO_2$ $C_6H_5CHOH-CH_2NO_2$

Acids   Acids   Acids   Acid

ESTERS   ESTERS   ESTERS   Hydrolysis

Reduction   Reduction   Reduction

$CH_2OH - CH_2NH_2$ $(CH_2OH)_2CHNH_2$ $(CH_2OH)_3CNH_2$ $C_6H_5CHOH-COOH$

Higher Fatty Acids

SOAPS OF AMINOHYDROXI COMPOUNDS

Heat

AMIDES

Nitromethane Tree (2)

Part II

$$CH_3NO_2$$

Cl_2	Reduction	$(CH_3)_2CO$	KOH NaOH	Acid Hydrolysis

CH_2ClNO_2 CH_3NHOH $(CH_3)_2C\!\!<^{CH_2NO_2}_{CH_2NO_2}$ $CH_2=N\!\!<^{O}_{ONa}$ NH_2OH

$CHCl_2NO_2$ CH_3NH_2

$$\underset{CH-CH=N}{\overset{NOH}{\|}}\!\!<^{O}_{OK}$$

CCl_3NO_2

C_2H_5ONa $HgCl_2$

$(C_2H_5O)_4C$ NH_3 $(C=NO)_2Hg$

$HN=C(NH_2)_3$

Aldehydes
&
Ketones

**Alkali Salts
of Nitroparaffins**

OXIMES

Reduction

DINITROPARAFFINS

AMINES

TABLE III

Properties of Nitromethane (2)

Molecular Weight...61

Boiling Point, ^{o}C.......................................101

Freezing Point, ^{o}C......................................-29

Flash point (Tagliabue open cup) ^{o}F....................95

Index of refraction 20°C............................1.3817

Wt. per U.S. gallon, lb..................................9.5

Color..water white

Odor...mild

Soly. in 100 c.c. water c.c. 9.10

Soly. of water in 100 c.c. nitroparaffin c.c. 2.2

Vapor press @ 20°C., mm. Hg 27.8

pH 0.01 M aq. soln. 6.12

pH water saturated with nitroparaffin................4.01

pH paraffin saturated with water 4.82

Surface tension at 20°C. dynes/cm......................37

Evaporation rate (1 butanol)...............................4

DUHRING LINE FOR
NITROMETHANE AND WATER

FIGURE 8

VAPOR PRESSURE
CURVE FOR
NITROMETHANE

WATER TEMPERATURE °C.
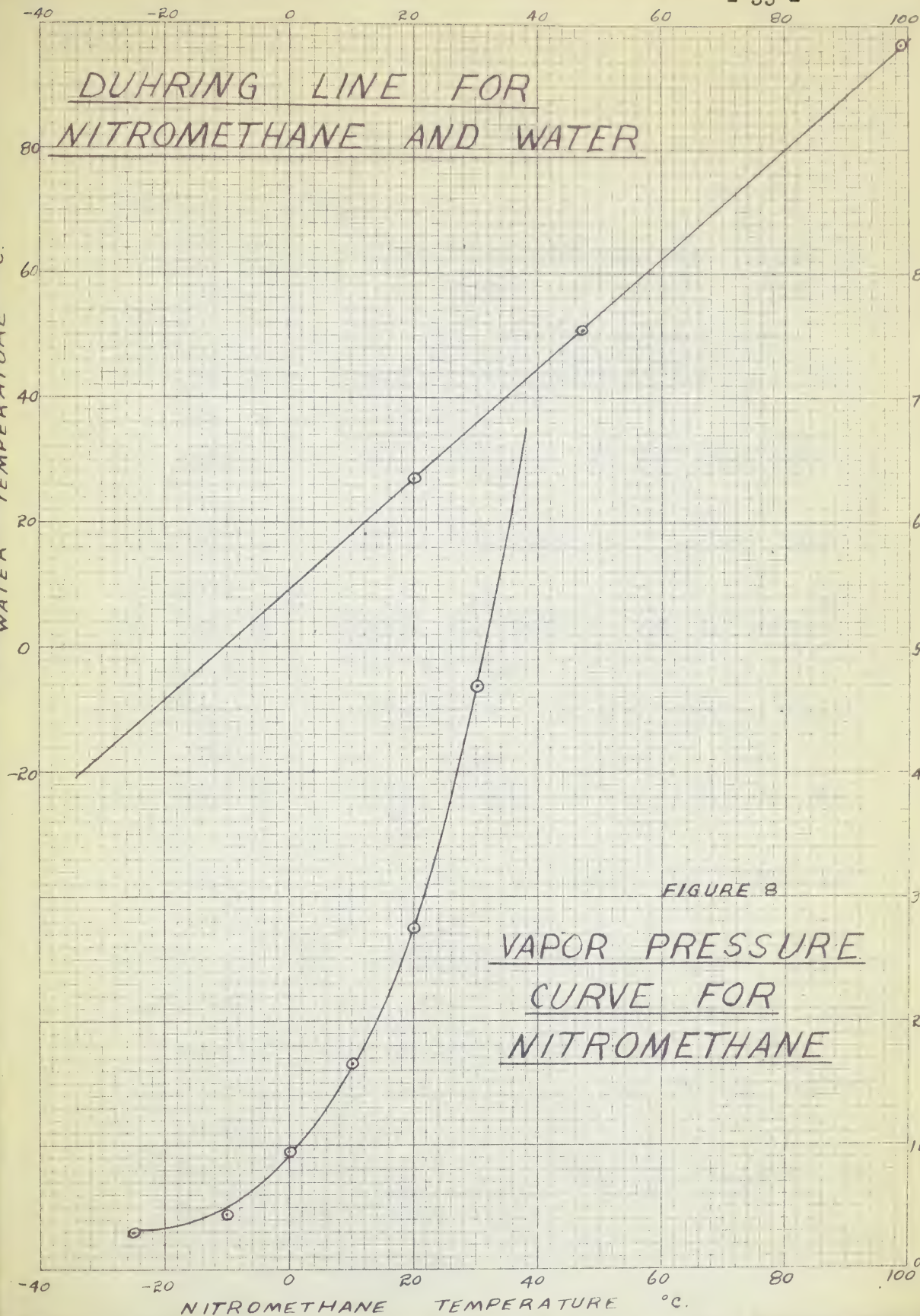
NITROMETHANE TEMPERATURE °C.
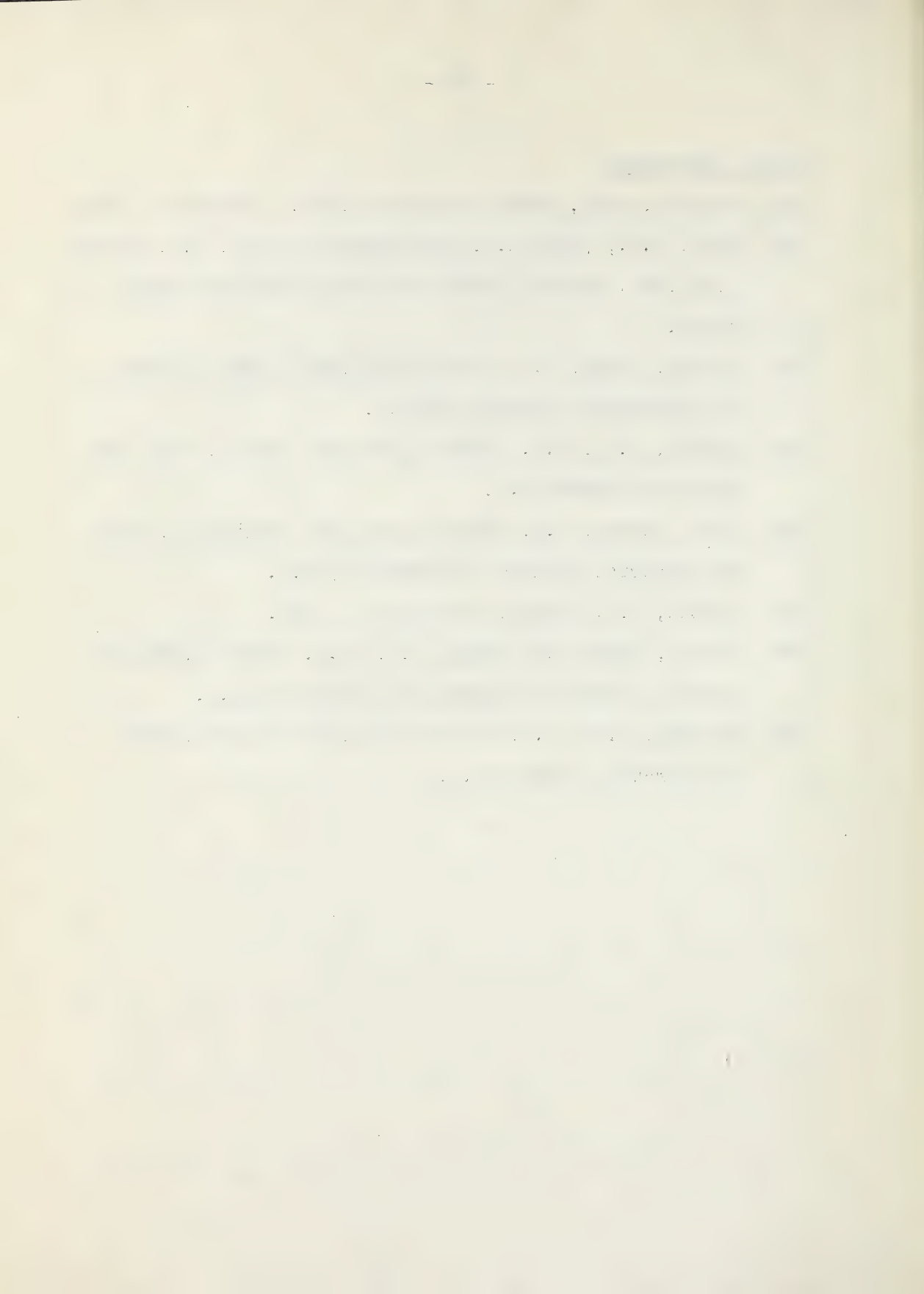
VAPOR PRESSURE mm. Hg.

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